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Citation	Chemical communications (2012), 48(36): 4317-4319
Issue Date	2012-03-08
URL	http://hdl.handle.net/2433/172232
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Type	Journal Article
Textversion	author

Chemical Communications

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Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

Communication

A doubly 2,6-pyridylene-bridged porphyrin-perylene-porphyrin triad

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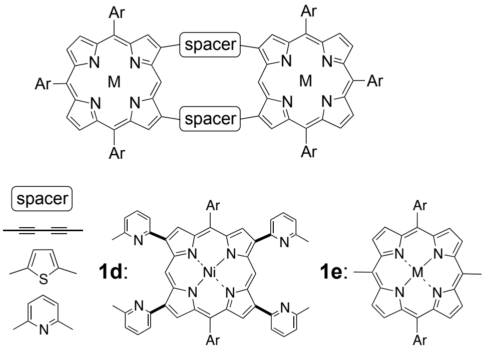
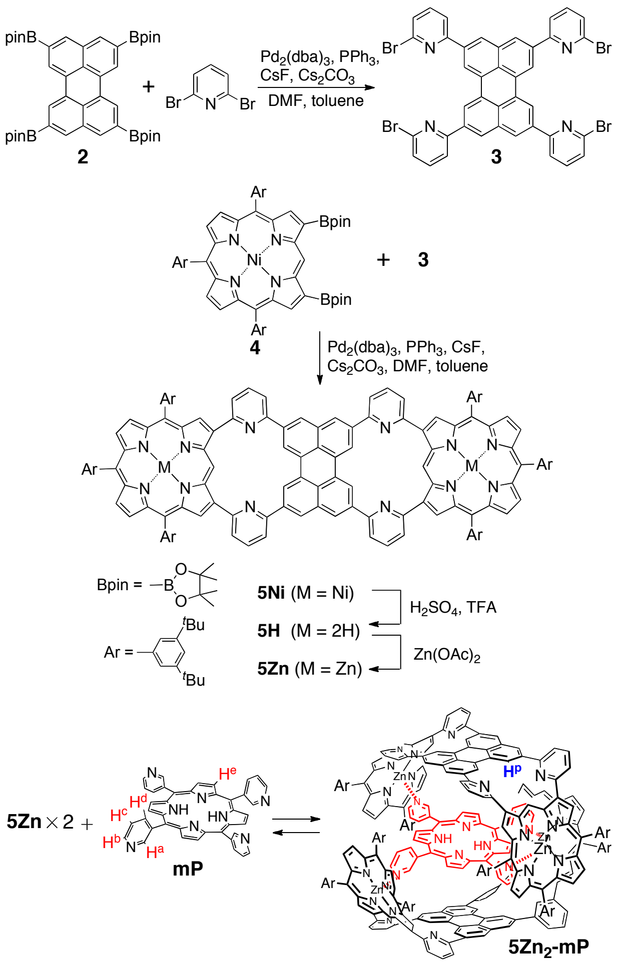
Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX
DOI: 10.1039/b000000x

A doubly 2,6-pyridylene-bridged porphyrin-perylene-porphyrin triad was synthesized via Suzuki–Miyaura cross coupling reaction, which captures a tetrakis(3-pyridyl)porphyrin guest in a 2:1 manner to form a supramolecular complex that undergoes photo-induced electron transfer.

Covalently linked multiporphyrin arrays have been extensively explored for their applications in photosynthetic models, sensors, molecular wires, nonlinear optical (NLO) materials, and so on.[1] Among these, we have recently explored iridium(I)-catalysed β-borylation reaction of porphyrins that provides β-borylated porphyrins selectively.[2] Using these β-borylated porphyrins we have developed various functional oligomeric porphyrin arrays including doubly β-to-β bridged porphyrin arrays **1a**, **1b**, **1c-d** and **1e** that have butadiyne-,[3] 2,5-thiophene-,[4] 2,6-pyridylene-[5] and 5,15-porphyrinylene-spacer,[6] respectively. Interestingly, these porphyrin arrays (**1a-d**) displayed large two-photon absorption (TPA) cross-section values owing to the effective π-conjugation between two porphyrins.[7]



We have also developed three-dimensional porphyrin ladders via combined reaction sequences of Ag(I)-promoted *meso-meso* coupling of porphyrins and Suzuki–Miyaura coupling.[6] Furthermore, the similar strategy allowed us to synthesize doubly 2,6-pyridylene-bridged bent porphyrin belts[7] and porphyrin barrels,[8] which exhibited C_{60}-encapsulating ability. As an extension of this strategy, we envisioned that insertion of a large aromatic spacer between a 2-pyridyl spacer would lead to modulation of molecular shape of porphyrin arrays in curvature and ring diameter. With this idea, we tried the synthesis of a doubly 2,6-pyridylene-bridged porphyrin-perylene-porphyrin triad as a prototype. Perylene is important and potential functional organic molecules that have been used in various applications such as field effect transistors (FETs), electrical conductors, and organic electroluminescence (EL) devices.[9] Interestingly, we have found that a triad zinc(II) complex can bind a tetrakis(3-pyridyl)porphyrin guest in a 2:1 manner, in which the efficient electron transfer takes place from the zinc(II) porphyrin host to the free base porphyrin guest.



Scheme 1. Synthesis of porphyrin-perylene-porphyrin hybrid triads and host-guest complexation of **5Zn** with **mP**.

The synthetic scheme of porphyrin-perylene-porphyrin triad **5** is shown in Scheme 1. 2,5,8,11-Tetraborylperylene **2**[10] was coupled with an excess amount of 2,6-dibromopyridine under Suzuki–Miyaura cross-coupling conditions to afford 2,5,8,11-tetrakis(6-bromopyrid-2-yl)perylene **3** in 50% yield, which is practically insoluble in common organic solvents. 5,10,15-Triaryl-2,18-diborylporphyrin nickel(II) complex **4**[2] was coupled with suspended **3**. Separation by gel permeation chromatography (GPC) and silica gel chromatography afforded the triad **5Ni** in 14% yield. High-resolution electrospay-ionization time-of-flight (HR-ESI-TOF) mass spectrum of the hybrid porphyrin dimer displayed the parent ion peak at m/z = 1209.0845 (calcd. for $C_{164}H_{160}N_{12}Ni_2$ = 1209.0868 $[M]^{2+}$). The ^1H-NMR spectrum of **5Ni** in $CDCl_3$ at room temperature was very broad but became sharpened at 60°C to exhibit one singlet peak and two doublet peaks for the β-protons at 9.78, 8.92 and 8.69 ppm, a singlet peak at 10.71 ppm for the *meso*-protons, two singlet peaks for the perylene protons at 8.69 and 8.41 ppm, and two doublets and one triplets for the pyridine protons at 8.09, 7.98 and 7.78 ppm. The structural assignment of perylene has been proved by ^1H-^1H NOESY technique (see Figure S4 in Supplementary Information; SI†).

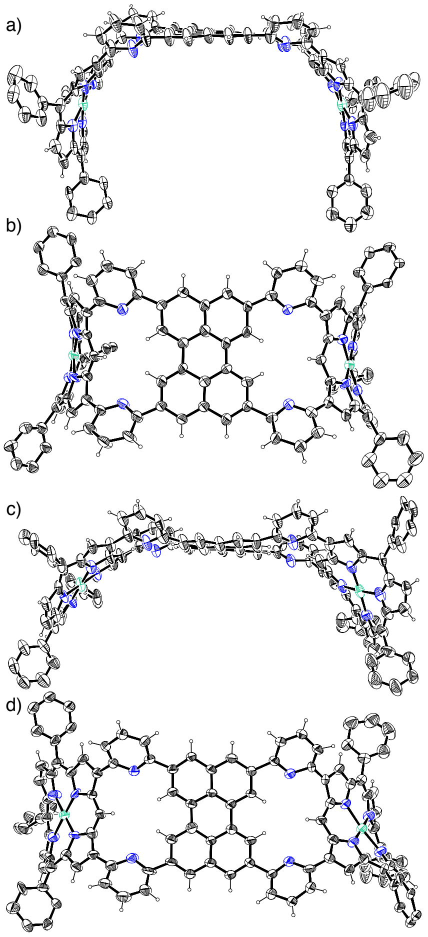


Figure 1. X-ray crystal structures of **5Ni**. (a) Side and (b) top view of triad A and (c) side and (d) top view of triad B. Substituents on phenyl groups are omitted for clarity. The ellipsoids are scaled to the 20% probability.

The single crystals of **5Ni** suitable for X-ray diffraction analysis were grown by slow vapour diffusion of acetonitrile into its chloroform solution (Figure 1).‡ The crystallographic asymmetric unit of **5Ni** contains two molecules (triads A and B) of different structures, both of which took belt-like *syn* conformations. The centre-to-centre distances between the nickel ions are 16.68 and 18.98 Å for triads A and B, respectively. The porphyrin moieties are tilted by 50.17, 59.43, 68.73 and 74.91° relative to the perylene mean planes. These facts indicate certain conformational flexibility for **5Ni**. In the solid state, triads A and B are alternatively stacked with their facing perylene parts closer at a distance of ca. 3.6 Å.†

Nickel complex was demetalated with H_2SO_4/TFA to give free base porphyrin dimer **5H**, which was then converted into the corresponding zinc(II) complex **5Zn** upon treatment with $Zn(OAc)_2$. The UV/Vis absorption spectrum of **5Zn** in CH_2Cl_2 are shown in Figure 2. The **5Zn** exhibits blue-shifted Soret band at 429 nm and Q bands at 554 and 596 nm as compared with those of reference 5,10,15-triaryl-2,18-dipyridylporphyrin zinc(II) complex **6Zn** (Soret band; 433 nm, Q bands; 557 and 598 nm).† These phenomena suggest the weak but distinct excitonic interaction between the porphyrin and perylene units.[11]

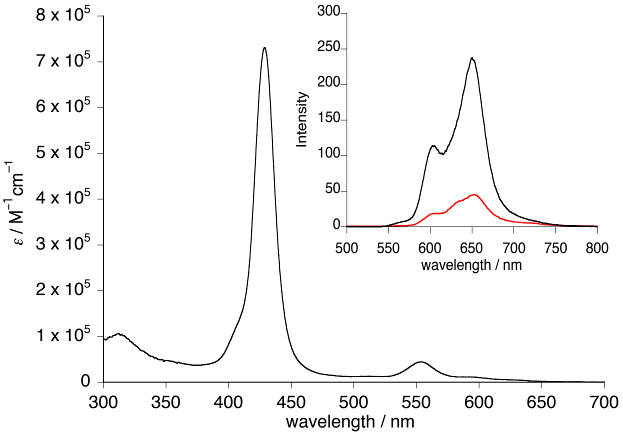


Figure 2. UV/vis absorption spectrum of **5Zn** in CH_2Cl_2. Inset: fluorescence spectra of **5Zn** (black) and **$5Zn_2$–mP** (red) excited at 437 nm in CH_2Cl_2.

The bent structure of **5Ni** and its conformational flexibility inspired us to examine the supramolecular interaction with tetrakis(3-pyridyl)porphyrin (**mP**).[12,13] Photometric titration experiments were conducted to determine the stoichiometry between **5Zn** and **mP** in CH_2Cl_2. Upon the addition of **mP** to the **5Zn** solution, the absorption intensities at 429 and 554 nm were found to decrease and that at 515 nm was seen to increase with isosbestic points at 437 and 562 nm. As shown in Figure S13,† a plot of the absorbance at 429 nm versus [**mP**] has an inflection point at [**mP**]/[**5Zn**] = 0.5. The Job's plot clearly supported a 2:1 stoichiometry (Figure S12†). The ion peak of the complex was successfully detected by HR-ESI-MS in a positive mode at m/z = 2740.2639 for $[\mathbf{5Zn_2}\text{–}\mathbf{mP} + 2H]^{2+}$ (calcd for $[C_{368}H_{346}N_{32}Zn_4]^{2+}$ = 2740.2713) (Figure S11†). These phenomena explain that **5Zn** and **mP** form a 2:1 complex. The ^1H NMR spectrum of the 2:1 mixture of **5Zn** and **mP** shows large complex-induced changes in chemical shifts for the signals corresponding to the pyridyl protons of **mP** as shown in Figure 3. These results clearly demonstrate the guest-binding ability of **5Zn**.

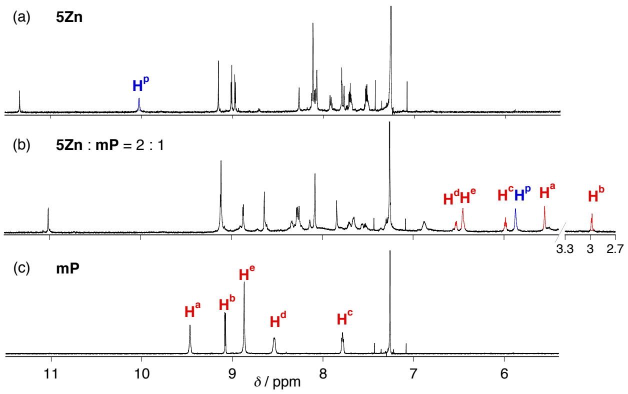


Figure 3. ^{1}H NMR spectra of (a) **5Zn**, (b) a mixture of **5Zn** and **mP** (2:1), and (c) **mP** in $CDCl_3$.

The steady-state fluorescence spectra of **$5Zn_2$–mP** are shown in the inset of Figure 2. Upon photoexcitation of **$5Zn_2$–mP** at 437 nm that corresponded to selective excitation at the zinc(II) porphyrin moieties, the complex exhibited reduced fluorescence from **5Zn** part. Importantly, the fluorescence from the **mP** was not detected. These data suggested the intracomplex electron transfer from the photoexcited **5Zn** to **mP**, while the excitation energy transfer is the most common process for zinc(II) free-base hybrid porphyrin pairs.[14] By cyclic and differential pulse voltammetry methods in CH_2Cl_2, the first reduction potential of **mP** and the first oxidation potential of **6Zn** were measured to be –1.40 and +0.39 V, respectively, with respect to the Ag/$AgClO_4$. The free energy calculated by the Rehm–Weller equation[15] indicates that the electron transfer from ^{1}**(5Zn)*** to **mP** is exothermic by –0.46 eV, while the free energy change associated with the excitation energy transfer is –0.15 eV.† The coordination interactions between the pyridyl groups with the Zn(II) centres render the zinc(II) porphyrins more electron-donating and the pyridyl-appended free base porphyrin more electron-accepting, which makes the intracomplex electron transfer more feasible.

In conclusion, we have synthesized the doubly 2,6-pyridylene-bridged porphyrin-perylene-porphyrin triad by Suzuki–Miyaura cross-coupling reaction. The ^{1}H-NMR, mass, and UV/Vis absorption spectra of this triad revealed the structural characterisation in solution, and the bent structure was observed in the solid state of **5Ni**. The supramolecular complex **$5Zn_2$–mP** lead to novel electro-photochemical properties. Investigation on perylene-inserted porphyrin nanobarrel is currently in progress.

This work was partly supported by Grants-in-Aid for Scientific Research (Nos. 19205006 (A), 23685030 for Young Scientists (A) and 20108006 "pi-Space") from the Ministry of Education, Culture, Sports, Science and Technology, Japan, and by JST PRESTO program. The authors thank Prof. H. Maeda and Dr. Y. Haketa (Ritsumeikan University) for MALDI-TOF MS measurement.

Notes and references

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† Electronic Supplementary Information (ESI) available: Experimental details of the synthesis and spectroscopic analytical data of new compounds. See DOI: 10.1039/b000000x/

‡ Crystallographic data for **5Ni**: $C_{164}H_{160}N_{12}Ni_2$, M = 2416.46, triclinic, space group P-1 (#2), a = 20.6104(4), b = 28.4361(5), c = 32.8677(6) Å, α = 113.2820(8), β = 98.5654(9), γ = 95.3241(9)°, V = 17251.5(6) Å^3, T = 93(2) K, Z = 4, reflections measured 165438, 49870 unique. The final R_1 was 0.0913 (>$2\sigma(I)$), and the final $_wR$ on F^2 was 0.2044 (all data), GOF = 0.974. CCDC 865051 contains the supplementary crystallographic data for this paper. The contributions to the scattering arising from the presence of the disordered solvents in the crystal were removed by use of the utility SQUEEZE in the PLATON software package.[16]

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